Conference Paper

# Heat Treatment Effect on Magnetic Properties of Finemet-Type Films

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## Abstract

A study of the heat treatment effect on the structure and magnetic properties of the amorphous and nanocrystalline Finemet-type thin films of the compositions $Fe_{73.9}Si_{13.2}B_{8.9}Nb_3Cu_1$ and $Fe_{72.5}Si_{14.2}B_{8.7}Nb_2Mo_{1.5}Cu_{1.1}$ were performed by means of X-ray diffraction, magneto-optical Kerr-microscopy, and magnetic properties measurement system. The heat treatment leads to magnetic anisotropy decreasing as a result of crystallization processes, which are heavily dependent on the alloy's composition.

**Keywords:** soft magnetic material, FINEMET, thin films, annealing

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## 1. Introduction

The alloy of composition $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$(Finemet) was announced by Yoshizawa *et al.* almost thirty years ago [1]. Since then Finemet-type alloys have attracted a great interest from both the scientific and applied points of view due to their excellent soft magnetic properties. A high saturation magnetization, low coercivity, and high permeability of the alloy are caused by a two-phase structure containing $\alpha$-Fe(Si) grains uniformly dispersed in a residual amorphous matrix, and are explained in the frame of the random anisotropy model (RAM) [2]. Additional interest to this kind of materials was caused after giant magnetoimpedance (GMI) discovery. High GMI effect in Finemet materials family can be a basis for the development of small magnetic field sensors and biosensors [3].

It is known that the grain structure of FINEMET alloys could be altered by doping of Cu and Nb atoms which effects the kinetics of $\alpha$-Fe(Si) grain formation and suppresses their growth, correspondingly. Using appropriate heat treatment of an amorphous alloy precursor and chemical composition variation, a control of nanocrystalline state is possible [4].

The necessity of the miniaturization of devices raised an interest in magnetic thin films. Among them, two types could be marked out: 1) amorphous magnetic thin films due to their low magnetic anisotropy and high electrical resistivity and 2) Finemet-type thin films, which have the potential application as a perspective medium for GMI microsensors [5].

In this work, the effect of annealing on the structure and magnetic anisotropy of the Finemet-type thin films of the conventional composition and doped by Mo has been studied.

## 2. Methods

Thin film samples of $Fe_{73.9}Si_{13.2}B_{8.9}Nb_3Cu_1$ and $Fe_{72.5}Si_{14.2}B_{8.7}Nb_2Mo_{1.5}Cu_{1.1}$ alloys were produced by means of high-frequency ion-plasma sputtering in Ar atmosphere. Initially, the pressure in a sputtering chamber was of $10^{-6}$ Torr and it increased to $10^{-3}$ Torr during the samples deposition. The thin films with thickness of 200 nm were deposited onto glass and monocrystalline Si (100) substrates. The latter was covered with the buffering $SiO_2$ layer of 100 nm. The deposition was held in a technical magnetic field of 100 Oe oriented parallel to substrates. Samples of 10x10 $mm^2$ and 4x5 $mm^2$ sizes were cut for X-ray powder diffraction (XRD) analyses and magnetic measurements, respectively. Thermal treatments of the samples were performed in the sputtering chamber at the temperatures of 350, 400, and 450°C for 30 minutes. In-plane technical magnetic field was applied in the same direction during annealing.

The film thicknesses were verified using Dektak150 stylus profilometer as a step height between the film surface and substrate. Investigation of the microstructure was performed by XRD using a PHILIPS X'PERT PRO automatic diffractometer operating at 40 kV and 40 mA, in theta–theta configuration, with a secondary monochromator with Cu-K$\alpha$ radiation ($\lambda$=1.5418Å) and a PIXcel solid state detector. More details on the method are described elsewhere [6]. Hysteresis loops in both easy magnetization axis (EA) and hard magnetization one (HA) were measured in-plane of the films by Evico magnetics GmbH magneto-optical Kerr effect (MOKE) microscope using an overview mode. Temperature dependencies were measured using magnetic properties measurement system MPMS XL7 from room temperature up to 425 °C with heating rate of 2 °C/min in the magnetic field of 100 Oe.

## 3. Results

MOKE hysteresis loops of $Fe_{73.9}Si_{13.2}B_{8.9}Nb_3Cu_1$ and $Fe_{72.5}Si_{14.2}B_{8.7}Nb_2Mo_{1.5}Cu_{1.1}$ thin films are shown in Fig. 1 as functions of an azimuthal angle ($\varphi$) between EA and field direction. There is a strong variation in the shape of hysteresis loops with the angle. For the film of conventional Finemet composition (Fig. 1a), hysteresis loop at $\varphi$ = 0° has a perfect square form that can indicate on a domain wall motion during the magnetization reversal process. Increasing azimuthal angle involves the hysteresis loop rounding-off, because the rotation of domain magnetization contributes to the magnetization reversal; for $\varphi$ = 90° only the rotation takes place. The thin film of Finemet alloy doped with Mo has a resembling behavior (Fig. 1b). However, $M_R/M_S$ ratio and non-zero value of coercivity for $\varphi$ = 90° denotes existence of the rotation

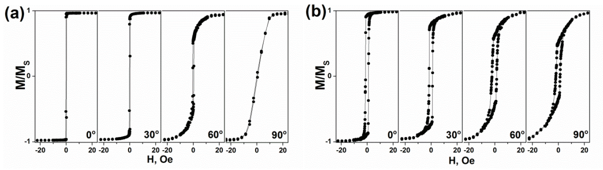


**Figure** 1: MOKE hysteresis loops at different azimuthal angles between EA and field direction for as-deposited films of $Fe_{73.9}Si_{13.2}B_{8.9}Nb_3Cu_1$ (a) and $Fe_{72.5}Si_{14.2}B_{8.7}Nb_2Mo_{1.5}Cu_{1.1}$(b) alloys.

magnetization together with domain wall motion. The observed hysteresis loops in dependence on the angle show that the thin films possess a uniaxial magnetic anisotropy. The magnetic anisotropy in the as-prepared films are induced by the technological field during the deposition as well as internal stresses in the film [7]. Let us note that coercivity of the thin film with Mo is bigger than that of the film of the conventional Finemet composition.

In Fig. 2 the magnetization dependencies on temperature are presented for the thin films of both compositions and for the ribbon of Finemet alloy doped by Mo. It is clearly seen that crystallization in the thin films starts earlier in comparison with the ribbon. The partial substitution Nb by Mo led to decrease of the Curie temperature of amorphous phase ($T_{Cam}$). Non-zero value of magnetization at the temperature higher $T_{Cam}$, as shown in the inset in Fig. 2, may be explained by the presence of small nanocrystallites in the as-prepared film of the alloy with Mo. For the purpose of verifying the structural state, the sample of Finemet composition with Mo was investigated by means of XRD methods. Fig. 3 shows XRD patterns of the film with Mo for annealing temperatures of 350 and 400-450 °C, which were chosen according to M vs. T dependence in order to get stress relaxed and nanocrystalline states, correspondingly. Amorphous halos for the as-prepared state and after annealing at 350 °C suggest roentgen-amorphous structure of the film. However, it does not except the presence of tiny crystallites, which size was estimated about 5 nm using the Scherrer formula. The crystallites can change the chemical composition of amorphous phase that in turn can lead to variation of its Curie temperature.

The fact that the as-prepared film possibly contains small nanocrystallites can be reflected on the hysteresis properties. Existence of such crystallites may explain the aforesaid peculiarity of the magnetization process for the film with Mo in Fig. 1b, since the crystallites act as a pinning center obstructing the domain wall motion. For this reason, the higher coercivity is observed for the film of alloy doped by Mo in comparison with the thin film of the conventional Finemet composition.

As stated above, in the thin films crystallization starts earlier than in ribbons of the identical composition in accordance with M vs. T curves in Fig. 2. These results are also confirmed by XRD data, where the crystallization peak after annealing at 450 °C is seen (Fig. 3). The grain size estimated from the peak is about 40 nm, which is bigger than expected in Finemet alloy. There are two possible explanations. First, the temperature of annealing 450 °C is overrated in comparison with the optimal temperature for the formation of nanocrystalline structure and realization of the best soft magnetic properties [8]. Second, the smaller atomic radius of Mo can be responsible for the increase in grain sizes as reported for the ribbon in Ref. [9].

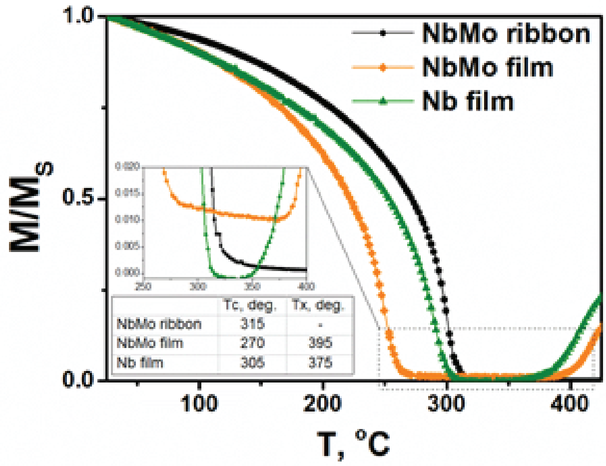


**Figure** 2: Temperature dependences of *M* for of $Fe_{73.9}Si_{13.2}B_{8.9}Nb_3Cu_1$ alloy film and of $Fe_{72.5}Si_{14.2}B_{8.7}Nb_2Mo_{1.5}Cu_{1.1}$alloy film and ribbon.

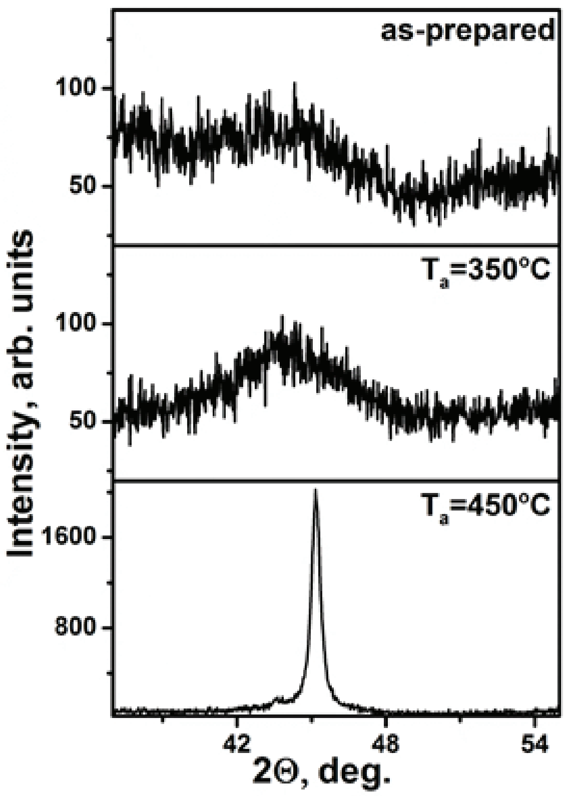


**Figure** 3: XRD patterns of the film of $Fe_{72.5}Si_{14.2}B_{8.7}Nb_2Mo_{1.5}Cu_{1.1}$alloy in as-prepared state and at different annealing temperatures.

For study of heat treatment effect, thin films of 4x5 mm$^2$ size were cut from the bigger one and were annealed at different temperatures in the presence of magnetic field. The influence of annealing on magnetic properties is shown in Figs.4 and 5. As-prepared state of the films is shown in Figs. 4a and 5a and is characterized by marked induced anisotropy, which value in common can be estimated as the area between

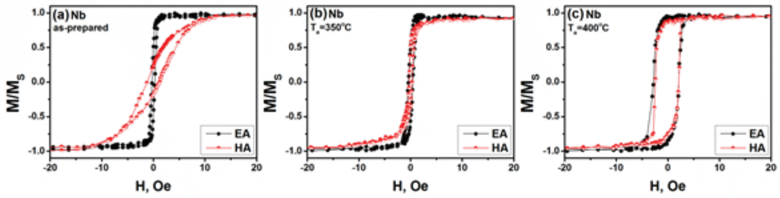


**Figure** 4: MOKE hysteresis loops along EA and HA for $Fe_{73.9}Si_{13.2}B_{8.9}Nb_3Cu_1$ film in as-prepared state (a) and after annealing at 350 (b) and 400 °C (c).

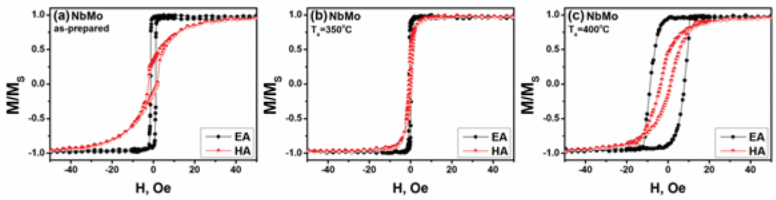


**Figure** 5: MOKE hysteresis loops along EA and HA for $Fe_{72.5}Si_{14.2}B_{8.7}Nb_2Mo_{1.5}Cu_{1.1}$ film in as-prepared state (a) and after annealing at 350 (b) and 400 °C (c).

the hysteresis loops corresponding to the EA ($\varphi$ = 0°) and HA ($\varphi$ = 90°). For the films of both compositions, annealing at 350 °C decreases the magnitude of the induced anisotropy field and coercivity as seen in Figs. 4b and 5b. It is connected with the anisotropy destruction by the diffusion motion of atoms, when the annealing temperature equals $T_{Cam}$and external field has no effect. There is difference in the hysteresis loops shape of the films of the conventional Finemet composition and doped by Mo after annealing at 400 °C when the onset of crystallization takes place. Fig. 4c shows that the anisotropy completely disappears in the film of the conventional composition. The temperature of 400 °C corresponds to early stage of crystallization as follow from the temperature dependence of magnetization in Fig. 2. The formed tiny crystallites obstruct domain wall motion that gives rise to coercivity increase. But crystalline phase is not enough for anisotropy inducing. For the film of Finemet alloy doped by Mo the magnetic anisotropy exists after annealing at 400 °C in comparison with the previously discussed film (Fig. 5c). The growth of grains, which are already presented in the as-prepared films, can promote induction of anisotropy. Moreover, magnetocrystalline anisotropy of the grains can contribute to the magnetization processes besides the induced one. Usually, it happens because the grains become large enough for efficient averaging of their magnetocrystalline anisotropy by exchange interactions within the frame work of RAM [2]. Magnetocrystalline anisotropy and related increase of the anisotropy dispersion led to coercivity increasing for both EA and HA.

## 4. Conclusion

Amorphous and nanocrystalline thin films of $Fe_{73.9}Si_{13.2}B_{8.9}Nb_3Cu_1$ and $Fe_{72.5}Si_{14.2}B_{8.7}Nb_2Mo_{1.5}Cu$ composition were studied by means of XRD, MOKE magnetometer techniques. The as-prepared thin films demonstrated uniaxial magnetic anisotropy induced by technological field during the deposition. Heat treatments led to decrease of the magnetic anisotropy field value as a result of diffusion motion of the atoms at the temperature between the Curie temperature of amorphous phase and crystallization temperature. At the annealing temperature of 400 °C, magnetic anisotropy is not induced for the film of conventional Finemet composition to compare with the film of alloy doped by Mo.

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